

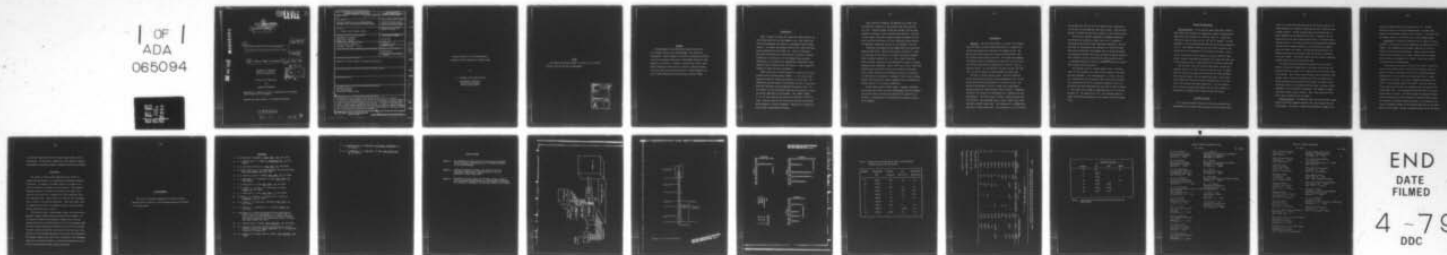
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ELEMENTAL ANALYSIS OF GAS CHROMATOGRAPHIC EFFLUENTS WITH AN IND--ETC(U)
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Elemental Analysis of Gas Chromatographic
Effluents With An Inductively Coupled Plasma

by

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Brief

The inductively-coupled plasma is evaluated as an element selective detector for gas chromatography.

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Abstract

The performance of the inductively-coupled plasma (ICP) as an element selective gas chromatographic (GC) detector is investigated. Special emphasis is placed on evaluating the ability of the ICP to perform simultaneous multielement analyses on each component of a mixture. In general, ICP detection limits, linear dynamic ranges and selectivities are shown to compare favorably with those which have been observed for the flame photometric detectors (FPD) and microwave-excited plasma detectors (MEPD).

Introduction

While a number of studies have shown that flame detectors can yield high sensitivity for some elements (1-4), they suffer from certain disadvantages with respect to simultaneous multielemental analysis. To achieve the reported sensitivities, conditions often must be optimized for each element (3). The use of molecular band heads for analysis can cause emission intensities to depend strongly on the structure (5) of the compound being analyzed. Additionally, the relatively low temperatures encountered in most chemical flames seriously limits the analysis of many non-metallic elements by atomic emission spectrometry.

Difficulties have also been reported in conjunction with the microwave-excited plasma detector (MEPD). In some cases, atomic emission intensities varied with molecular structure (6-8). Recombination reactions appear to be extensive (6) and, in some cases, molecular band heads have been employed for analysis (6,8). As with flames, the use of molecular band heads for analysis can limit the general applicability of the method. For example, Dagnel et. al. (8) have reported that when the CS band head at 2576 \AA is used, a detection limit of 0.2 ng of sulfur from CS_2 was observed which degraded to 10 μg for thiophene. Additionally, thioglycolic acid yielded no observable CS emission.

From a practical viewpoint, the MEPD may also suffer from the formation of deposits on the inside of the excitation cell (6, 9-12). Molecular oxygen (10,12) and nitrogen (12) have been employed as scavenger gases to prevent these deposits. However, a recent report stated that internal etching and deposition still occur within the excitation cell (13) indicating the desirability of completely eliminating the need to view through a cell wall.

Preliminary investigations have demonstrated that inductively-coupled plasma atomic emission spectrometry (ICP-AES) is a sensitive technique for the analysis of several non-metallic elements found in organic compound (14, 15). These studies found that atomic emission transitions can be employed for analysis of carbon, hydrogen, boron, phosphorus, iodine, sulfur and silicon, eliminating problems often associated with the use of molecular band heads. Only a slight variation in the elemental response with structure was observed for the majority of compounds. While several diatomic species were observed, the results suggested that the formation of diatomic species is not a major interference.

In the current study a direct reader, a computer controlled data acquisition system, and a gas chromatograph have been combined with an ICP system to evaluate the quantitative capabilities of ICP-AES as a technique for the simultaneous multielement analysis of GC effluents.

Experimental

Apparatus. The ICP system (Figure 1) consists of the plasma torch, RF supply, optical system with detectors, a computer controlled data acquisition system and a GC sampling system. The plasma torch and RF supply have been previously described (14). The following modifications were made: the coolant tube employed for elemental analyses extended 10.5 cm above the top of the load coil and the sample tube was replaced with 7 mm O.D., 1 mm I.D. capillary tubing. All observations were made 9 mm above the load coil, viewing the plasma discharge through the coolant tube.

The optical system contains a model EU-700 GCA McPherson (Acton, Massachusetts) 350 mm scanning monochromator and a 66-100 Jarrell-Ash (Waltham, Massachusetts) 1.5 M direct reader. The McPherson monochromator contains a single pass Czerny-Turner mounted grating with 1180 lines/mm, blazed at $5000 \text{ \AA}^{\text{C}}$. A Hamamatsu (Middlesex, New Jersey) R777 photomultiplier is employed with this monochromator. The direct reader contains a concave grating ruled 1180 lines/mm. The wavelength range is 2000 to $8000 \text{ \AA}^{\text{O}}$ first order and 2000 to $4000 \text{ \AA}^{\text{O}}$ second order. The dispersion is $5.45 \text{ \AA/mm}^{\text{O}}$ first order and $2.7 \text{ \AA/mm}^{\text{O}}$ second order. The resolution is $0.2 \text{ \AA}^{\text{O}}$ or better.

The entrance slit and exit slits are 200 and 75 μm , respectively. All PM tubes are RCA (Harrison, New Jersey) 1P28A. Light from the plasma is directed into the direct reader by a first surface mirror.

The low level currents (nanoamps to microamps) produced by the PM tubes are converted to high level (1-10 v) voltages by electrometers based on FET input operational amplifiers. The outputs from the electrometers are interfaced to a Hewlett-Packard (Palo Alto, California) 2116C computer with an analog multiplexer for choosing the channel to be read, an analog to digital converter and a hardware clock for controlling the data acquisition rate. All program algorithms are written in CONVERS[©] (details are available on request from the authors).

The sampling system is a Varian (Walnut Creek, California) model 1520 GC equipped with a model D2-1866 Automatic Linear Temperature Programmer. The column employed is a 6 foot, 1/8 inch O.D. column packed with 8% carbowax 1540 on 80/100 mesh firebrick. The interface between the GC column and a modified version of a previously described demountable ICP torch (16) is shown in Figure 2. The output of the column is connected directly to a 1/16 inch Swagelok "T". One branch of the "T" is the "makeup" argon (0.9 L/min) and the third branch goes to the sample tube of the plasma torch.

Results and Discussion

Emission Spectra. In the spectral region from 1900 to 8000 Å⁰, most intense lines produced by non-metallic elements originated from upper levels with energies less than 8 ev (Table 1). These transitions also have gA values of $1.0 \times 10^8 \text{ sec}^{-1}$ or greater. The one exception is the H_α line (6562.9 Å⁰) which has an excitation energy of 12.1 ev. The intensity of the H_α line also raises a question concerning the role of frequency in ICP excitation processes. The H_α line is very intense in this relatively low power (~800 W) 27 MHz plasma. However, Greenfield and McGeachin (17) report that this line is not detected in their 7.5 MHz plasma until the power exceeds 5KW.

Near IR atomic lines are observed from bromine, chlorine and fluorine, however, all these lines are relatively weak. No atomic lines for nitrogen or oxygen are observed between 1900 and 8000 Å⁰. The excitation energies for the theoretically most intense atomic lines (7468.3 and 7772.0 Å⁰ for N and O respectively) are 12.0 and 10.7 ev for nitrogen and oxygen respectively. This may account for the absence of observable atomic lines for these elements in the spectra of compounds which contain nitrogen and oxygen.

Diatomic Molecules

If a large and variable fraction of the atoms produced in the high temperature excitation region recombine to form diatomic mole-

cules, at or below the observation zone in the plasma, then the observed response for a specific element may vary as a function of the original molecule. Several diatomic species are observed when organic compounds are introduced into the ICP. In general, only diatomic species with bond energies greater than 5 eV produced strong emission spectra. The vertical position of maximum observed response for the carbon containing species (C_2 , CN, CO and CS) are approximately the same as for carbon. The vertical emission profiles of diatomic molecules not containing carbon (NH and OH) are observed to be very diffuse. The emission spectra of these species increased slightly toward the top of the coolant tube.

The most intense band spectra are produced by CO, CN and CS. However, observation of band spectra from these molecules does not mean that diatomics account for a large fraction of the total carbon in the plasma. The relative carbon responses for acetonitrile, ethyl alcohol, ethyl acetate and thiophene show that even though the CO, CN and CS populations are increased when oxygen, nitrogen or sulfur containing species are introduced into the plasma, the atomic carbon population is not significantly decreased. This suggests strongly that these diatomic species contain only a small fraction of the total carbon introduced into the plasma.

Detection Limits. ICP detection limits and linear dynamic ranges (Table 2) generally compared favorably with those reported for the FPD and MEPS. For metallic elements and non-metallic elements with

relatively intense atomic lines (Fe, Pb, Sn, C, H, I and Si), detection limits are in the low nanogram range. For these same elements, linear dynamic ranges are 10^3 or greater. Detection limits for bromine, chlorine, and fluorine are in the microgram range.

Selectivity. An important capability of any element selective detector is its ability to provide independent determination of each element. The simultaneous multielement capability of the ICP is especially suited to this application. Figure 3 shows the simultaneous readout obtained at the carbon, hydrogen and tin channels when a mixture of tetramethyl tin, benzene, toluene and p-xylene are eluted from the chromatograph.

To evaluate the selectivity of the ICP GC detector, selectivity ratios versus atomic carbon at $2478.6 \text{ \AA}^{\circ}$ were determined (Table 3). Selectivity ratios were found to be limited by background changes brought about by the introduction of large quantities of organic compounds to the plasma. Two types of background changes were observed. For wavelengths longer than 3000 \AA° , which are not close to any molecular band heads, the background generally decreases for large sample sizes. For wavelengths shorter than 3000 \AA° , the background tends to increase. The observed negative background changes can be attributed to an overall decrease in plasma intensity caused by a decrease in the power coupling efficiency to the plasma as the result of impedance changes in the plasma brought about by the introduction of the sample. Positive background changes can be attributed

to scattered light either from the intense atomic carbon lines or band spectra. In both cases, selectivity ratios should be improved considerably by employing automatic background correction techniques.

Conclusions

The results of these studies demonstrate that the ICP is capable of being utilized as a simultaneous multielement selective GC detector. As opposed to the MEPD, oxygen or nitrogen do not need to be added to the plasma to reduce deposits. While deposits sometimes formed on the inside of an extended ICP coolant tube, these were not found to be a problem since they formed well above the observation zone. Unlike flames, all analyses can be performed with a single set of operating conditions. Since only atomic lines are employed for analysis, the problems sometimes associated with diatomic band heads can be avoided.

ICP detection limits, linear dynamic ranges, and selectivities generally compare favorably with those for the FPD and MEPD. For the metallic elements and non-metallic elements with relatively intense atomic lines, detection limits are in the low nanogram range, and linear dynamic ranges and selectivities are both 10^3 or greater. The major limitation currently associated with the technique is the absence of atomic nitrogen and oxygen lines and the low intensity of the bromine, fluorine and sulfur lines. Extension of the wavelength range into the Vacuum UV promises to allow the determination of sulfur (17) and possibly nitrogen, oxygen and bromine.

Acknowledgement

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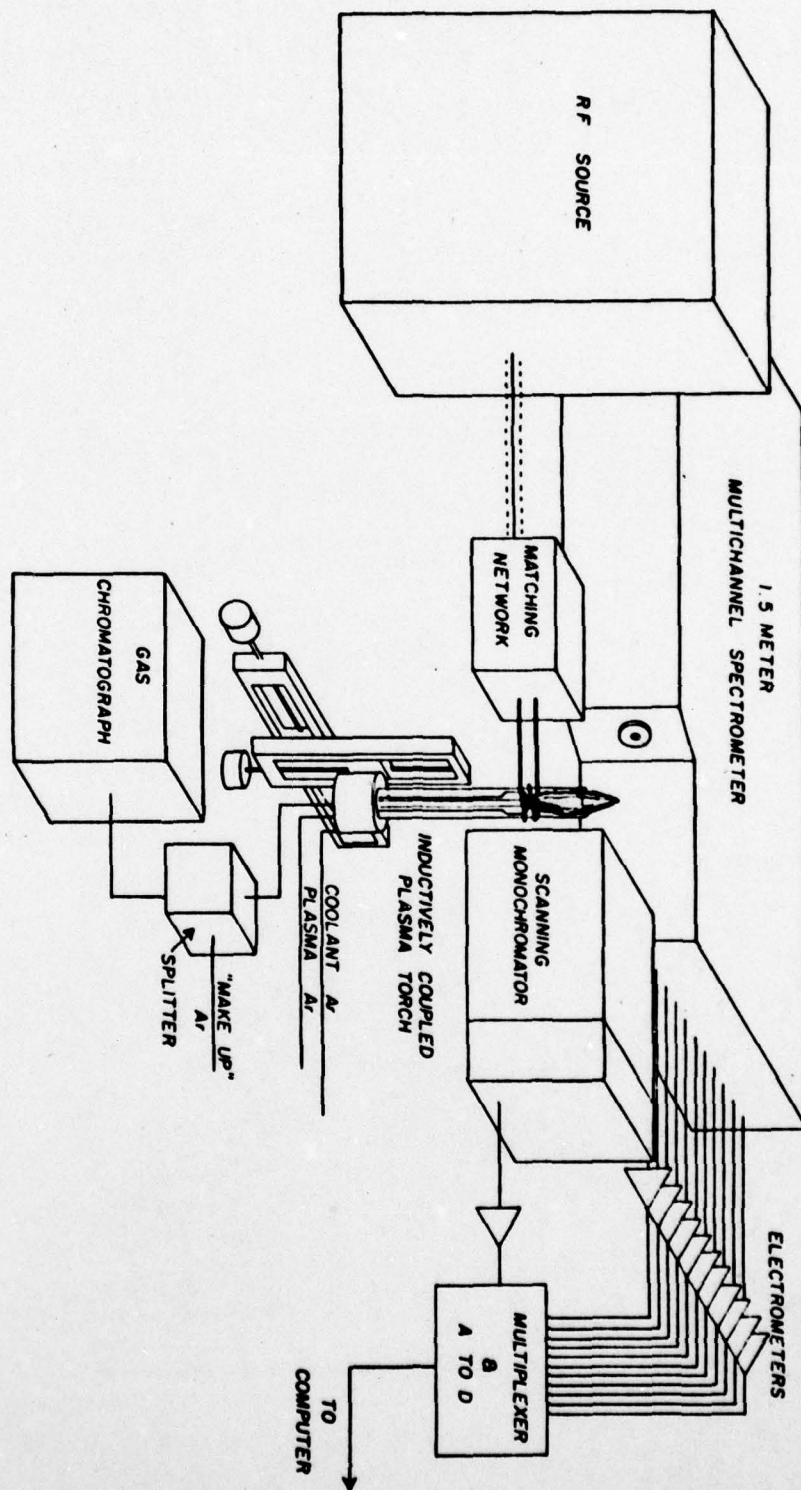
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FIGURE CAPTIONS

- Figure 1. The experimental system used for evaluating the performance of the inductively coupled plasma as an elemental detector for gas chromatography.
- Figure 2. Interface coupling GC effluent into modified ICP torch. Note normal sample tube is replaced with a 0.1 mm I.D. capillary to reduce dead volume.
- Figure 3. Simultaneous analog readouts of the atomic carbon, hydrogen, and tin channels obtained during the chromatographic separation of a mixture of tetramethyl tin, benzene, toluene, and p-xylene.



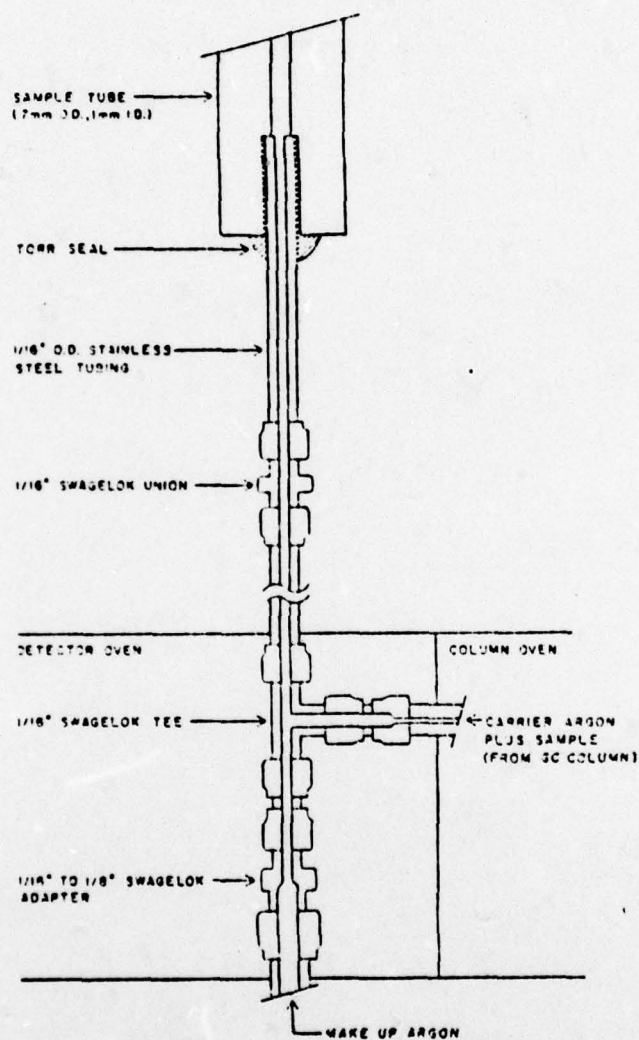
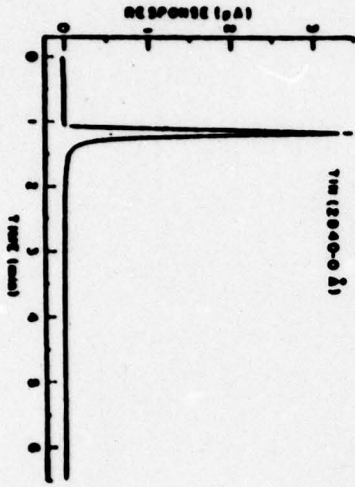
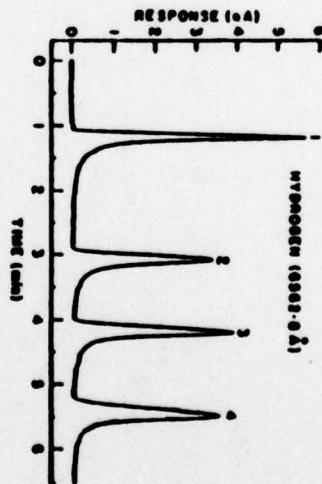
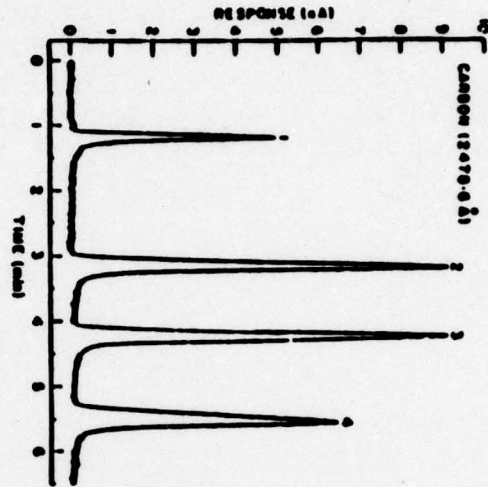


Figure 11. GC to ICP interface.

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PEAK	SAMPLE WEIGHT (mg)		
	C	H	O
1) TETRAETHYLMETHANE	20	6.0	0.5
2) BENZENE	01	3.1	0
3) TOLUENE	50	5.7	0
4) p-XYLENE	00	0.1	0

Table 1. Observed most intense atomic lines for non-metallic elements between 1900 and 8000 Å.

Element	Wavelength (Å)	Relative Intensity	gA (10^8 sec^{-1})	Excitation Energy (ev)
B	2497.7	610	4.8	5.0
Br	7005.7	<1	-	-
C	2478.6	100	1.0	7.7
Cl	7256.7	<1	0.8	10.6
F	6348.5	<1	0.7	14.7
J	6562.8	110	7.9	12.1
I	2061.6	20	-	-
P	2136.2	200	11	7.2
S	1900.3	4	0.003	6.5
Si	2516.1	1420	6.1	5.0

Table 2. Comparison of Observed ICP detection limits and Linear Dynamic Ranges with Flame Emission and Microwave Emission Plasma GC Detectors

Element	Atomic Wavelength(A)	ICP	Detection Limit (ng)				Linear Dynamic Range		
			Air-Rich	H-Rich ^a	Argon MEPP ^d	ICP	FPD	MEPP ^d	
Br	7005.7	2x10 ⁵	-	-	-	poor	-	1x10 ³	
C	2478.6	12	4x10 ^{3a}	1x10 ⁴	-	1x10 ³	1x10 ^{2a}	1x10 ³	
Cl	7256.7	7x10 ³	-	-	12	1x10 ²	-	1x10 ²	
F	6348.5	1x10 ⁶	-	-	70	poor	-	-	
H	6562.8	5.5	-	-	-	1x10 ³	-	-	
I	2061.6	24	10 ^b	-	22.4	1x10 ³	1.4x10 ^{2b}	1x10 ²	
Si	2516.1	0.8	0.4 ^c	-	-	5.10 ³	10 ^c	-	
Fe	3719.9	5.9	2 ^c	0.8	-	2.10 ⁴	1x10 ^{2a}	-	
Pb	2170.0	33	40 ^b	5	-	1x10 ³	1x10 ^{3a}	-	
Sn	2840.0	0.9	5 ^b	5	-	1x10 ⁴	1x10 ^{2a}	-	

^aAue and Hill (1973).

^bSevcik (1976, p. 161).

^cGutsche and Herrmann (1971).

^dDagnall et al (1972b).

Element	Selectivity Ratio		
	ICP	FDP ³	MEPD ⁷
Cl	60	-	30
H	3×10^3	-	-
I	1×10^3	-	-
Si	3×10^4	-	20
Fe	1×10^3	1×10^4	-
Pb	3×10^3	1×10^3	-
Sn	3×10^4	2×10^3	-

Table 3. Comparison of ICP selectivities with those for the FDP and MEPD.

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